

(12)

(21) 2 321 353

(51) Int. Cl. 7: B27K 3/34, B27K 3/40

(22) 28.09.2000

(30) 199 47 182.7 DE 30.09.1999

(71)

WACKER-CHEMIE GMBH,
Hanns-Seidel-Platz 4
D-81737, MÜNCHEN, XX (DE).

(72)

WIMMER, THOMAS (DE).
IMSGARD, FINN (DK).

(74)

MCFADDEN, FINCHAM

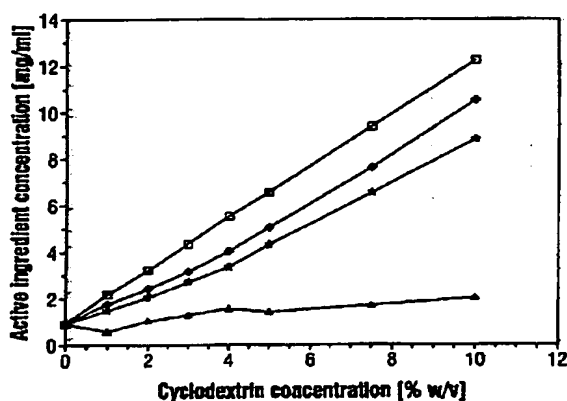
(54) PRODUITS DE PRESERVATION DU BOIS, PROCESSUS DE PREPARATION ET UTILISATION DE CES PRODUITS

(54) WOOD PRESERVATIVES, PROCESSES FOR THEIR PREPARATION AND THEIR USE

(57)

An aqueous wood preservative or a wood preservative which is dilutable in water, is a complex composed of a cyclodextrin derivative containing a hydrophobic active ingredient. Compared with known aqueous wood preservatives or wood preservatives which are dilutable in water, the wood preservative exhibits an improved depth of penetration and an improved activity against timber pests.

Solubility of tebuconazole



—●— methyl-α-cyclodextrin
—●— methyl-β-cyclodextrin
—●— methyl-γ-cyclodextrin
—●— hydroxypropyl-β-cyclodextrin

10/537192

JC06 Rec'd PCT/PTO 02 JUN 2005

**WOOD PRESERVATIVES, PROCESSES FOR THEIR
PREPARATION AND THEIR USE**

ABSTRACT OF THE DISCLOSURE

An aqueous wood preservative or a wood preservative which is dilutable in water, is a complex composed of a cyclodextrin derivative containing a hydrophobic active ingredient. Compared with known aqueous wood preservatives or wood preservatives which are dilutable in water, the wood preservative exhibits an improved depth of penetration and an improved activity against timber pests.

BACKGROUND OF THE INVENTION

The present invention relates to wood preservatives, processes for their preparation, and their use.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an aqueous wood preservative or a wood preservative which is dilutable in water, which, compared with known aqueous wood preservatives or known wood preservatives which are dilutable in water, shows an improved penetration depth and an improved efficacy against timber pests.

The above object is achieved according to the present invention by a wood preservative which comprises a complex composed of a cyclodextrin derivative comprising a hydrophobic active ingredient.

The wood preservative according to the invention may be present as a ready-to-use aqueous solution, such as, for example, as an impregnating solution, glaze, color glaze or primer.

Further, it may also be present in the form of an aqueous concentrate which is brought to the use concentration by the end user by adding water.

It may furthermore be present as a solid wood preservative which is soluble in water.

The cyclodextrin derivatives in the wood preservative according to the invention are preferably selected from the group of the alkylated, hydroxyalkylated, acylated, branched and sulfoalkyl-ether-substituted α -, β - or γ -cyclodextrins.

The cyclodextrin derivatives are preferably selected from the group of the alkylated α -, β - or γ -cyclodextrins and hydroxyalkylated α -, β - or γ -cyclodextrins.

Especially preferred are the cyclodextrin derivatives which are selected from the group of the alkylated α -, β - or γ -cyclodextrins.

Particularly preferred are the cyclodextrin derivatives which are selected from the group of the methylated α -, β - or γ -cyclodextrins.

The complexed hydrophobic active ingredient is preferably a hydrophobic fungicide or a hydrophobic insecticide.

The active ingredient which is particularly preferably used is a mixture of various fungicides and/or insecticides.

The fungicide is preferably a fungicide from the group of the triazoles, tolylfluanid (N-dichlorofluoromethylthio- N',N'-dimethyl-N-p-tolylsulfamide), dichlorofluanide (N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfamide), IPBC (3-iodopropargyl N-butylcarbamate), isothiazolinones (N-octylisothiazolin-3-one) and 4,5-dichloro-N-octylisothiazolin-3-one.

It is particularly preferably a fungicide selected from the group consisting of propiconazole (1-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole), tebuconazole ((RS)-1-(4-chlorophenyl)-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)pentan-3-ol), azaconazole (1-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl)-methyl)-1H-1,2,4-triazole), fenbuconazole (4-(4-chloro-

phenyl)-2-phenyl-2-(1H-1,2,4-triazol-1-ylmethyl)-butyronitrile) and triadimenol ((1 RS,2 RS;1 RS,2 SR)-1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol), or 4,5-dichloro-N-octylisothiazolin-3-one. It is particularly preferably a fungicide selected from the group consisting of propiconazole or tebuconazole.

The insecticide is preferably a synthetic pyrethroid (such as, for example, cypermethrin, deltamethrin, permethrin, alphas-methrins), bifenthrin, fipronil, a benzeneurea derivative (such as, for example, hexaflumuron, teflubenzuron or flufenoxuron), a phosphoric ester (such as, for example, phoxim, parathion, fenitrothion, trichlorphon or dichlorphos), or a carbamate (such as, for example, propoxur, pirimicarb or aldicarb).

It is especially preferably cypermethrin, deltamethrin, permethrin or bifenthrin.

An aqueous wood preservative formulation according to the invention comprises water and, preferably, 0.01-2% by weight of hydrophobic active ingredient and, preferably, 1-20% by weight of cyclodextrin derivative, but preferably 0.5-1.5% by weight of hydrophobic active ingredient and 3-

16% by weight of cyclodextrin derivative. The balance up to 100% by weight is water. All percents by weight are based upon the total weight of the aqueous wood preservative formulation.

An aqueous wood preservative concentrate according to the invention comprises water and, preferably, 1-5% by weight of hydrophobic active ingredient and, preferably, 5-70% by weight of cyclodextrin derivative, especially preferably 2-6% by weight of hydrophobic active ingredient and 20-50% by weight of cyclodextrin derivative. The balance up to 100% by weight is water. All percents by weight are based upon the total weight of the aqueous wood preservative concentrate.

A solid wood preservative which is soluble in water comprises, preferably, 2-20% by weight of hydrophobic active ingredient and 50-98% by weight of cyclodextrin derivative, especially preferably 5-10% by weight of hydrophobic active ingredient and 70-95% by weight of cyclodextrin derivative.

The wood preservative according to the invention may furthermore comprise the following in the use concentrations

which are customary in each case (as a rule, approximately 0.001-5% by weight):

Bactericides, for example chloromethylisothiazolinone, methylisothiazolinone, aldehydes (for example 0.001%-0.2% by weight).

Boron compounds such as, for example, boric acid, borax.

Binders such as, for example, dispersible and emulsifiable synthetic resins (for example, polyvinyl acetate, polyester resin, acrylates, silicone resin).

Wetters.

Small amounts of solubilizers (approximately 0.01-2% by weight): alcohols, glycols, glycol ethers.

Anticorrosives.

Thickeners.

UV stabilizers.

Desiccants.

Colorants.

Pigments.

pH regulators.

However, the above-described aqueous CD complexes on their own are also effective as wood preservatives. The invention therefore also relates to the use of complexes of a CD derivative and a hydrophobic active ingredient as wood preservative, complexes of the already-mentioned derivatives with the already-mentioned hydrophobic active ingredients preferably being used.

The cyclodextrin/active ingredient complexes are produced by processes which are known per se, such as, for example, those described in J. Sejtli, "Cyclodextrin Technology", Kluwer Academic Publishers, 1988, p. 86 et seq.

For example, the cyclodextrin/active ingredient complexes may be prepared by stirring or shaking aqueous solutions of cyclodextrin derivatives with the active ingredient or the solutions of the active ingredient at temperatures of 10-80°C. Customary stirrers or dispersers are used for stirring. If appropriate, cosolvents such as, for example, lower alcohols, acetone, glycols and ethyl acetate may be employed in this process.

In a further method of preparing the complexes, the cyclodextrin derivatives are made into a paste with water in

a weight ratio of 6:4 to 9:1 and the paste is kneaded together with the active ingredient for approximately 10-200 minutes at 20°-80°C. The paste can be dried, for example in vacuo, to give solid wood preservatives according to the invention. The paste may furthermore be diluted with water to the desired application time.

Moreover, the cyclodextrin derivative and the active ingredient may be dissolved in a joint organic solvent, such as, for example, C₁-C₆-alcohols, C₃-C₆-ketones, ethyl acetate, methyl acetate or glycols. The solvent may subsequently be eliminated by drying, for example in vacuo. This gives, as a rule, solids which can be dissolved in water.

If the liquid wood preservatives according to the invention are dried to obtain a solid wood preservative according to the invention, conventional methods such as, for example, spray-drying or drying in vacuo are employed.

The wood preservatives in solid form can be processed for example by granulating, pelletizing, compacting, sieving, screening, tableting or packaging in water-soluble films.

Moreover, the invention relates to a method of preparing an aqueous wood preservative, wherein a solid wood preservative comprising a complex of a hydrophobic active ingredient and a cyclodextrin derivative is dissolved in water.

The invention furthermore relates to a method of protecting wood and timber materials, wherein wood or a timber material is treated with an aqueous formulation comprising a hydrophobic active ingredient and a cyclodextrin derivative, and subsequently dried.

Treatment is accomplished by means of methods known per se such as by means of atomizing, painting on, spraying or impregnating methods such as dipping, immersing, and the pressure, vacuum and double-vacuum methods.

A wood preservative formulation according to the invention exhibits unexpected advantages compared with known formulations which can be diluted with water. In the formulations according to the invention, lower active ingredient limits (determined as specified in DIN EN 113) have been found than in known formulations which are dilutable in water, both after thermal treatment and after

leaching. In particular the lower limits after leaching with water are entirely unexpected since a person skilled in the art would expect that the active ingredients would be more rapidly leached, due to the solubilization with cyclodextrins, thus leading to higher limits.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and features of the present invention will become apparent from the following detailed description considered in connection with the accompanying drawings which disclose several embodiments of the present invention. It should be understood, however, that the drawings are designed for the purpose of illustration only and not as a definition of the limits of the invention.

In the drawings, FIG. 1 shows that tebuconazole can be solubilized in water with the aid of methylated or hydroxypropylated cyclodextrins;

FIG. 2 shows that propiconazole can be solubilized in water with the aid of methylated cyclodextrins; and

FIG. 3 shows that bifenthrin can be solubilized in water with the aid of methylated cyclodextrins.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

EXAMPLES

The examples which follow are intended to illustrate the invention in greater detail. All percents are by weight unless specified otherwise.

EXAMPLE 1: Determination of the phase solubility diagrams of tebuconazole with various cyclodextrin derivatives

Among the cyclodextrin derivatives to be tested (products of Wacker-Chemie GmbH), quantities corresponding to 10.0 g of anhydrous substance are measured into a 100 ml volumetric flask and made up to the mark with 0.1-molar phosphate buffer (K_2HPO_4/KH_2PO_4). By diluting this 10% strength (w/v) stock solution, solutions are prepared whose concentrations range from 1% to 10% (w/v). Pure 0.1-molar phosphate buffer is used as comparison. 1-ml aliquots of the cyclodextrin derivative solution are treated with approx. 30 mg of tebuconazole and shaken for 48 hours at room

temperature. The samples are subsequently subjected to microfiltration (0.2 μ m filter). The tebuconazole concentration in the clear filtrates is determined by HPLC.

The results are shown in FIG. 1. It can be seen that tebuconazole can be solubilized in water with the aid of methylated or hydroxypropylated cyclodextrins

EXAMPLE 2: Determination of the phase solubility diagrams of propiconazole with various cyclodextrin derivatives

The experiments were carried out analogously to Example 1 using propiconazole.

The results are shown in FIG. 2. It can be seen that propiconazole can be solubilized in water with the aid of methylated cyclodextrins; and

EXAMPLE 3: Determination of the phase solubility diagrams of bifenthrin with various cyclodextrin derivatives

The experiments were carried out analogously to Example 1 using bifenthrin.

The results are shown in FIG. 3. It can be seen that bifenthrin can be solubilized in water with the aid of methylated cyclodextrins.

EXAMPLE 4: Preparation of a wood preservative formulation A (fungicidal wood preservation)

55 g of anhydrous methyl- α -cyclodextrin are dissolved in 945 ml of water. After addition of 3.0 g of tebuconazole and 3.0 g of propiconazole, the solution is warmed to 50°C, and the active ingredients are dissolved in the course of 3 hours with the aid of a disperser. This gives a clear solution which constitutes a ready-to-use wood preservative formulation with an active ingredient content of 0.6% by weight.

EXAMPLE 5: Preparation of a wood preservative formulation B (fungicidal wood preservation)

80 g of anhydrous methyl- β -cyclodextrin are dissolved in 920 ml of water. After addition of 2.0 g of tebuconazole, 2.0 g of propiconazole and 2.0 g of IPBC, the mixture is stirred for approximately 8 hours at 30°C. This

gives a clear solution which constitutes a ready-to-use wood preservative formulation.

EXAMPLE 6: Preparation of a wood preservative formulation C (insecticidal wood preservation)

100 mg of cypermethrin are dissolved in 100 ml of a 4% strength (w/w) aqueous solution of methyl- β -cyclodextrin. The pure solution constitutes a ready-to-use wood preservation formulation.

Wooden cubes which have been impregnated with this solution are not attacked by termites.

EXAMPLE 7: Preparation of a wood preservation formulation D (fungicidal and insecticidal wood preservation)

15 g of anhydrous methyl- β -cyclodextrin are dissolved in 985 ml of water. After addition of 0.6 g of tebuconazole, 0.9 g of propiconazole and 0.06 g of bifenthrin, the mixture is stirred for approximately 20 hours at 25°C. This gives a clear solution which constitutes a ready-to-use wood preservation formulation.

Compared with untreated timber materials, timber materials which have been impregnated with this solution are attacked less by wood-discoloring, wood-destroying fungi and wood-destroying insects (*Hylotrupes bajulus*).

EXAMPLE 8: Preparation of a wood preservation
formulation concentrate

22 g of methyl- β -cyclodextrin are dissolved in 85 g of water. After addition of 0.5 g of tebuconazole, 1.0 g of propiconazole and 0.08 g of bifenthrin, the mixture is stirred for approximately 20 hours at 40°C. This gives a clear solution which constitutes a wood preservation formulation concentrate. Dilution with water 1/10 (v/v) gives a clear, ready-to-use wood preservative formulation.

EXAMPLE 9: Spray-drying of a wood preservative
formulation

The solution of Example 4 is dried in a Niro laboratory dryer with the following parameters.

Dry air temperature: 210°C

Exhaust air temperature: 105°C

Type of atomization: 2-substance nozzle

The resulting powder has a residual moisture of 1.5% by weight. The active ingredient content was determined by HPLC: 4.81% by weight of tebuconazole, and 4.72% by weight of propiconazole.

The powder can be redissolved in water. At suitable concentration, this gives a ready-to-use wood preservative.

EXAMPLE 10: Use of wood preservative against insects

Wooden test pieces are fully impregnated with a solution of 1 g of cypermethrin and 25 g of methyl- β -cyclodextrin in 74 ml of water. The wooden test pieces treated thus were subjected to a test as specified in DIN EN22 (Hylotrupes bajulus). The mortality rate of the larvae was 87%.

EXAMPLE 11: Depth of penetration

Wooden test pieces (spruce: 250 x 60 x 40 mm) were treated in an immersion bath with formulation A (according to the invention) or formulation B (comparative example). To test the depth of penetration of the formulation, test specimens of approximate thickness 5 mm (5 x 60 x 40 mm)

were sawn out at right angles to the longitudinal axis of the wooden test pieces after the latter had dried. The test specimens were sterilized by gamma-irradiation, and, after incubation with the blueing fungus (*Aureobasidium pullulans*), incubated for 3 weeks at 23°C and an atmospheric humidity of 65%. No fungal growth was observed in the penetration zone of the formulation, while the untreated core was stained by the fungus.

TABLE 1 gives the composition of formulations A and B (Form. A and Form. B) and the parameters determined on the treated wood.

TABLE 1:

	Composition	UF [kg/ m ³]	UAI [kg/ m ³]	DOP [mm]
Form. A (Invention)	0.25% propiconazole	28.5	0.143	4
	0.25% IPBC			
	2.5% methyl- α -cyclodextrin			
	97% water			
Form. B (Comparison)	0.35% propiconazole	20.8	0.146	2
	0.35% IPBC			
	0.5% ethoxylated nonylphenol			
	6.5% Berol 278			

	1% N-methylpyrrolidone			
	91.3% water			

UF = Uptake of formulation of the wooden test pieces

UAI = Uptake of active ingredients

DOP = Depth of penetration

Despite a comparable uptake of active ingredients, the formulation according to the invention exhibits deeper penetration into the wood.

EXAMPLE 12: Efficacy test: wood-discoloring fungi

Three formulations were compared.

Formulation C: Solution of the active ingredients in Varsol 60 (hydrocarbons with a low aromatic content).

Formulation D: Emulsion of the active ingredients in an aqueous solution of 0.6% ethoxylated nonylphenol, 6.5% Berol 278 and 1.5% N-methylpyrrolidone.

Formulation E: Solution of the active ingredients in 4% methyl- β -cyclodextrin in water.

Active ingredients in formulation: 1:1 mixture (w/w) of propiconazole and IPBC.

Concentrations (total active ingredients): 0.05%, 0.10%, 0.20%, 0.30% (w/w).

Wooden disks (pine; diameter: 50 mm, height: 15 mm) are immersed into the wood preservative solution and dried in the air. After drying, the disks are stored for 1 week at 80°C. After the disks had been placed on a suitable nutrient medium, they are sterilized by gamma-irradiation and, after incubation with the test fungi, incubated for 3 weeks at 23°C and an atmospheric humidity of 65%.

TABLE 2 shows the results: (active ingredient concentration at which no fungal growth on the test specimen was observed).

TABLE 2:

Test fungus	Form. C (Comparison: in solvent)	Form. D (Comparison: as emulsion)	Form. E (Invention: formulated with cyclodextrins)

Aureobasidium pullulans	0.20%	0.10%	0.05%
----------------------------	-------	-------	-------

The results show advantageous lower use concentrations of the fungicides when using formulation C according to the invention for the blueing fungus (Aureobasidium pullulans).

EXAMPLE 13: Limits as specified in DIN EN 113 (wood-destroying fungi)

Formulation 1: Formulation which is dilutable in water, active ingredients are emulsified (comparative example)

0.6%	Ethoxylated nonylphenol	(emulsifier)
6.5%	Berol 278	(emulsifier)
1.5%	N-Methylpyrrolidone	(cosolvent)
1.2%	Propiconazole	(active ingredient)
0.9%	Tebuconazole	(active ingredient)
0.5%	IPBC	(active ingredient)
88.8%	Water	

Formulation 2: Formulation which is dilutable in water, solution of active ingredients in aqueous CD solution (wood preservative according to the invention)

1.2%	Propiconazole	(active ingredient)
0.9%	Tebuconazole	(active ingredient)
0.5%	IPBC	(active ingredient)
25%	Methyl- β -cyclodextrin	
72.4%	Water	

Wooden test pieces of standardized dimensions (15 x 25 x 50 mm) were fully impregnated by the vacuum method, additionally subjected to a thermal treatment (1 week at 80°C) or leaching in water (72 hours under running water) and exposed to the attack of wood-destroying Basidiomycetes. After 16 weeks, the weight loss of the wooden test pieces which is caused by the fungi is determined.

An acceptable efficacy is defined as an identified weight loss of < 3%.

TABLE 3 shows the active ingredient concentration in kg active ingredient/m³ wood at which the above criterion was met.

TABLE 3: LIMITS - ACTIVE INGREDIENT CONCENTRATIONS

	Comparison	Comparison	Invention	Invention
Test fungus	Form. 1 after thermal treatment	Form. 1 after leaching	Form. 2 after thermal treatment	Form. 2 after leaching
Coniophora	4.4 kg/m ³	6.6 kg/m ³	3.65 kg/m ³	6.3 kg/m ³

puteana				
Coriolus	15.0 kg/m ³	14.0 kg/m ³	9.6 kg/m ³	9.5 kg/m ³
versicolor				

Accordingly, while a few embodiments of the present invention have been shown and described, it is to be understood that many changes and modifications may be made thereunto without departing from the spirit and scope of the invention as defined in the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An aqueous wood preservative or a wood preservative which is dilutable in water, which comprises
a complex composed of a cyclodextrin derivative containing a hydrophobic wood preservative active ingredient.
2. A wood preservative as claimed in claim 1,
wherein the cyclodextrin derivative is selected from the group consisting of an alkylated α -, β - or γ -cyclodextrin, a hydroxyalkylated α -, β - or γ -cyclodextrin, an acylated α -, β - or γ -cyclodextrin, a branched α -, β - or γ -cyclodextrin and a sulfoalkyl-ether-substituted α -, β - or γ -cyclodextrin.
3. A wood preservative as claimed in claim 2,
wherein the cyclodextrin derivative is selected from the group consisting of an alkylated α -, β - or γ -cyclodextrin and a hydroxyalkylated α -, β - or γ -cyclodextrin.
4. A wood preservative as claimed in claim 3,

wherein the cyclodextrin derivative is selected from the group consisting of an alkylated α -, β - or γ -cyclodextrin.

5. A wood preservative as claimed in claim 4,
wherein the cyclodextrin derivative is selected from the group consisting of a methylated α -, β - or γ -cyclodextrin.

6. A wood preservative as claimed in claim 1,
wherein the hydrophobic active ingredient is selected from the group consisting of a hydrophobic fungicide, a hydrophobic insecticide, and mixtures thereof.

7. A wood preservative as claimed in claim 1,
wherein the hydrophobic active ingredient is a mixture selected from the group consisting of a mixture of fungicides, a mixture of insecticides, and mixtures thereof.

8. A wood preservative as claimed in claim 6,
wherein the fungicide is a fungicide selected from the group consisting of triazoles, tolylfluanid (N-dichloro-fluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide), dichlorofluanide (N-dichlorofluoromethylthio-N',N'-dimethyl-

N-phenylsulfamide), IPBC (3-iodopropargyl N-butylcarbamate), isothiazolinones (N-octylisothiazolin-3-one) and 4,5-dichloro-N-octylisothiazolin-3-one.

9. A wood preservative as claimed in claim 8,

wherein the fungicide is a fungicide selected from the group consisting of propiconazole (1-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole), tebuconazole ((RS)-1-(4-chlorophenyl)-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)pentan-3-ol), azaconazole (1-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole), fenbuconazole (4-(4-chlorophenyl)-2-phenyl-2-(1H-1,2,4-triazol-1-ylmethyl)butyronitrile), triadimenol ((1 RS,2 RS;1 RS,2 SR)-1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol), and 4,5-dichloro-N-octylisothiazolin-3-one.

10. A wood preservative as claimed in claim 6,

wherein the insecticide is selected from the group consisting of a synthetic pyrethroid, bifenthrin, fipronil, a benzeneurea derivative, a phosphoric ester, and a carbamate.

11. A wood preservative as claimed in claim 10,

wherein the insecticide is selected from the group consisting of cypermethrin, deltamethrin, permethrin and bifenthrin.

12. An aqueous wood preservative formulation comprising 0.01-2% by weight of hydrophobic wood preservative active ingredient;

1-20% by weight of cyclodextrin derivative; and the balance up to 100% by weight of water; with the weight percent of each ingredient based upon the total weight of the preservative formulation.

13. A wood preservative concentrate comprising 1-5% by weight of hydrophobic wood preservative active ingredient;

5-70% by weight of cyclodextrin derivative; and the balance up to 100% by weight of water; with the weight percent of each ingredient based upon the total weight of the preservative concentrate.

14. A water-soluble solid wood preservative comprising 2-20% by weight of hydrophobic wood preservative active ingredient;

50-98% by weight of cyclodextrin derivative; with the weight percent of each ingredient based upon the total weight of the preservative.

15. A wood preservative as claimed in claim 1, which furthermore comprises

a compound selected from the group consisting of bactericides, boron compounds, binders, wetters, solubilizers, anticorrosives, thickeners, UV stabilizers, desiccants, colorants, pigments, and pH regulators.

16. A method of preparing a wood preservative as claimed in

claim 1, comprising

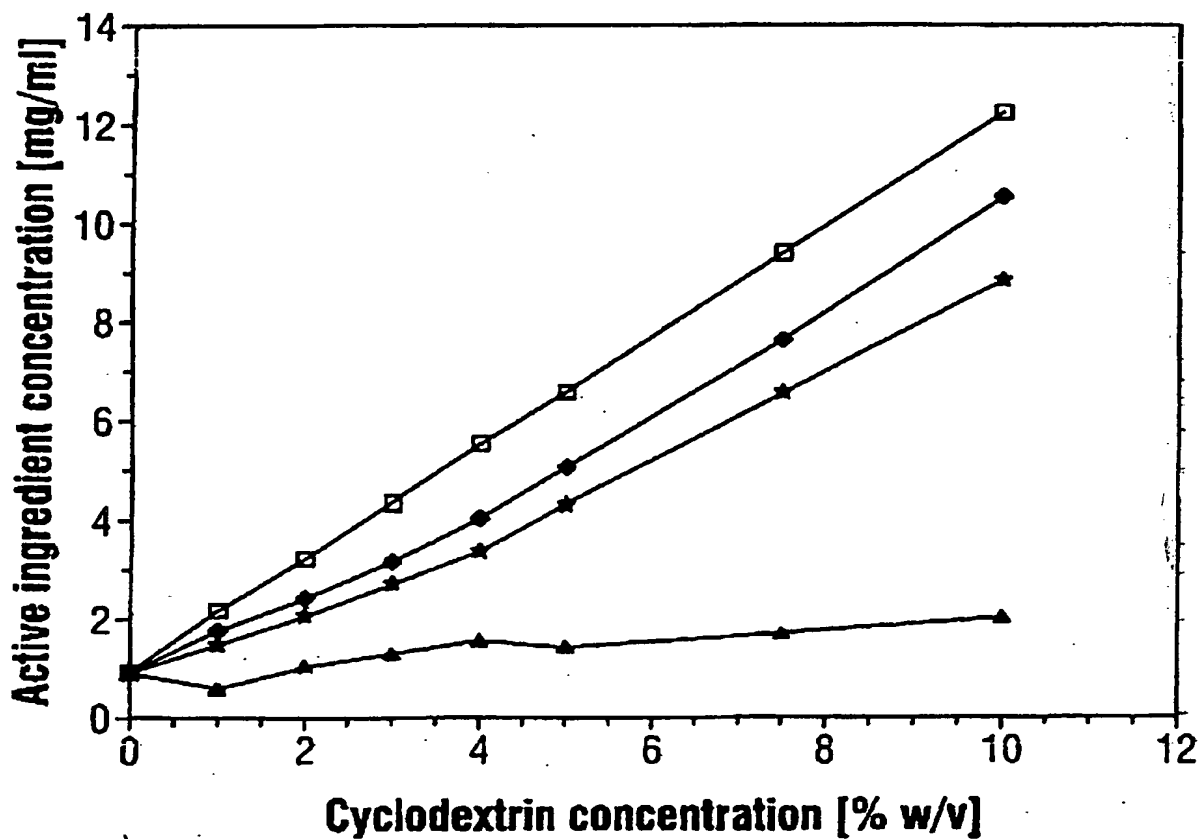
reacting a cyclodextrin derivative with a wood preservative active ingredient to form a complex of the cyclodextrin derivative with the active ingredient.

17. A method of preparing an aqueous wood preservative formulation as claimed in claim 12, comprising

dissolving a solid wood preservative comprising a complex of a hydrophobic wood preservative active ingredient and a cyclodextrin derivative in water.

18. A method of protecting wood and timber materials,
comprising

treating wood or a timber material with a wood
preservative as claimed in claim 1.

Fig. 1**Solubility of tebuconazole**

- methyl-α-cyclodextrin
- methyl-β-cyclodextrin
- ▲— methyl-γ-cyclodextrin
- ★— hydroxypropyl-β-cyclodextrin

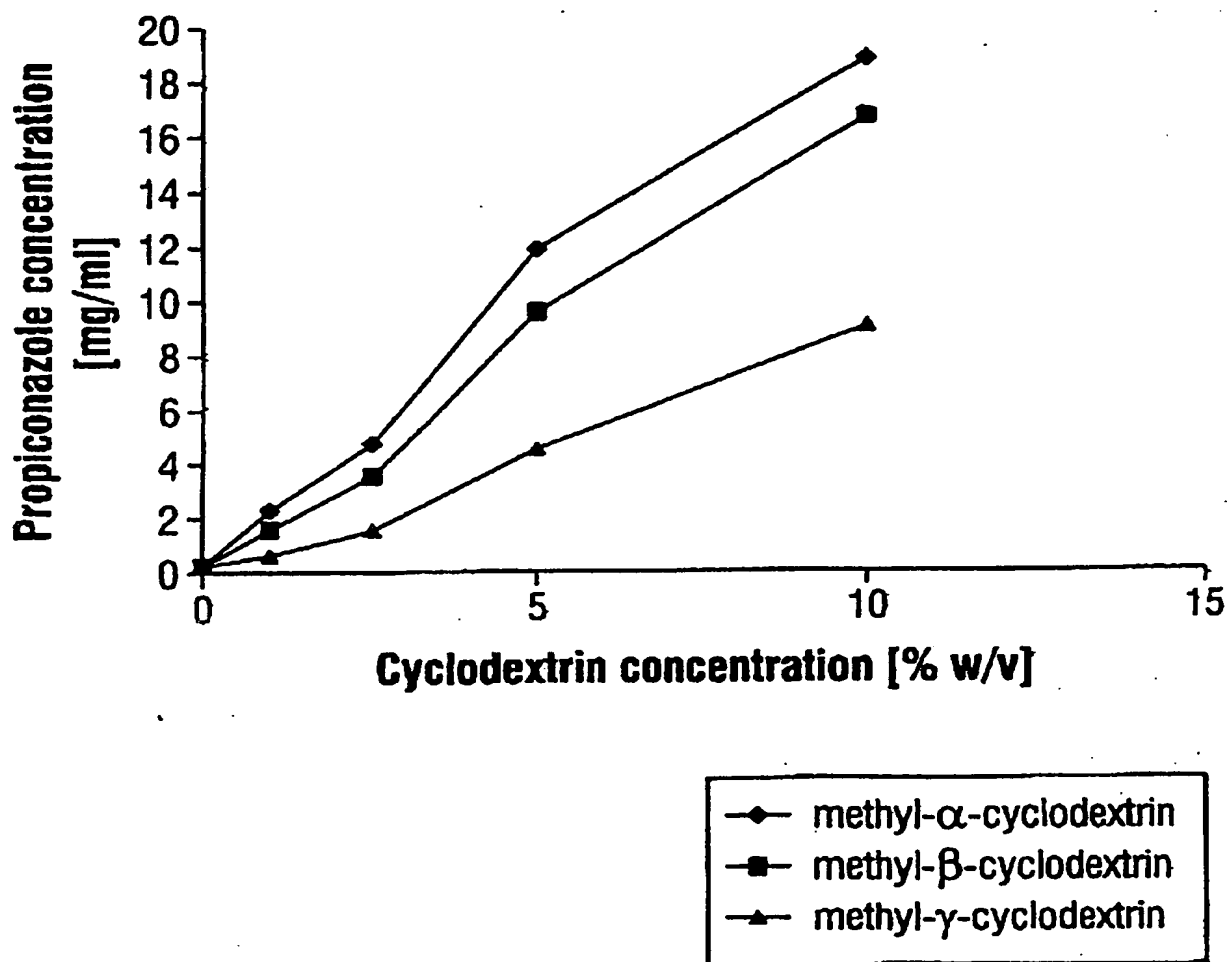
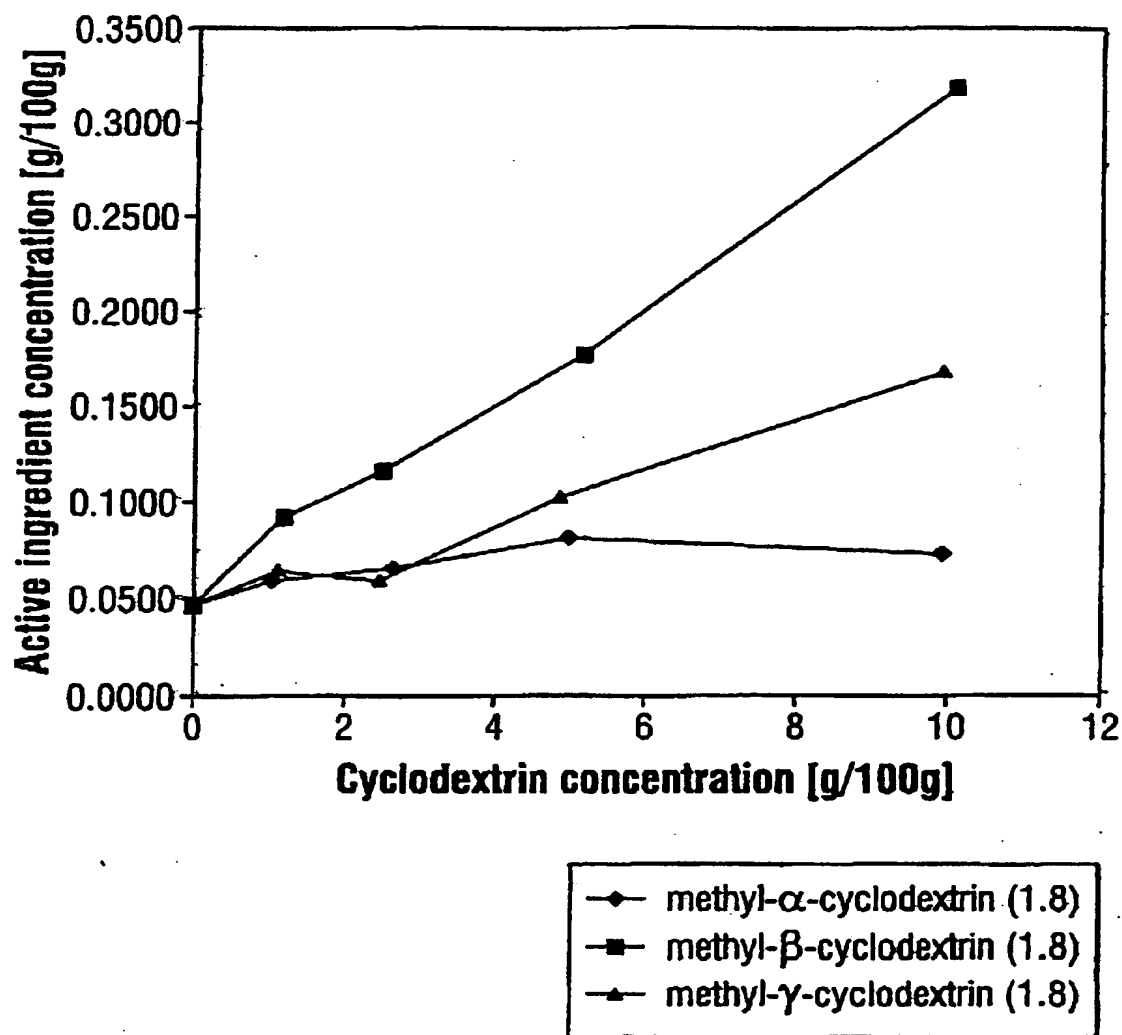
Fig. 2**Solubility isotherm of propiconazole**

Fig. 3**Solubility of bifenthrin**

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.